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# TECHNICAL REPORT

*1 July 1967-30 June 1968*

## MATERIALS SCIENCES PROGRAM



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UNIVERSITY OF MARYLAND  
CENTER OF MATERIALS RESEARCH  
COLLEGE PARK, MARYLAND

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ANNUAL TECHNICAL REPORT

SUBMITTED TO THE  
ADVANCED RESEARCH PROJECTS AGENCY  
OF THE  
DEPARTMENT OF DEFENSE

CONTRACT SD-101

July 1, 1967 to June 30, 1968

by

CENTER OF MATERIALS RESEARCH  
UNIVERSITY OF MARYLAND  
COLLEGE PARK, MARYLAND

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## SECTION I

### INTRODUCTION

This report summarizes the extensive program of research in Materials Sciences at the University of Maryland during the period 1 July 1967 through 30 June 1968. Faculty from the Departments of Chemistry, Physics, Molecular Physics, Chemical Engineering and Mechanical Engineering share this effort. Support for this program is derived from several government and military agencies. A specific listing of these sponsors can be found in Section VII. A key portion of the funding is from ARPA (Contract SD-101) and is administered through the Center of Materials Research. These funds are used in direct research support for purchase of equipment, and for graduate student, research associate, and faculty support. The funds also provide indirect research support through the establishment of a number of central facilities which are available to all materials science research workers.

The research effort is described in detail in Section II. The individual projects have been grouped into seven general areas of research. The faculty member responsible for each project is designated, and the sources of funds for a particular project are indicated.

Lists of participating faculty, research associates, and graduate students are provided in subsequent sections. Section VI is a complete listing of the publications which have resulted from the research program.

SECTION II  
RESEARCH PROGRAMS IN MATERIALS SCIENCES

A. LASER SCIENCE AND TECHNOLOGY

1. Intensity Fluctuations in High Stabilized CW Gas Lasers (Korenman)

NASA, ARO, ARPA

The intensity fluctuations in a highly stabilized CW gas laser were studied in the threshold region of operation, in order to test current models of laser operation. In particular the relatively smooth, spread out threshold for this single mode laser enabled us to quantitatively confirm the adequacy of single-parameter laser models. Photon counting techniques were the principal investigative tool but analog correlation techniques were also used. The work included measurements on zero time three and four photon correlations as well as measurements on the time diffusion of the laser intensity correlation function.

Present efforts are devoted to applying the techniques developed to measurements of higher correlations in fluids near a critical point. It is anticipated that further applications, such as measurements of phonon lifetimes and studies of molecular diffusion in fluids will follow.

2. Fluctuation and Correlation Phenomenon (Alley)

NASA, ARO, ARPA

Fluctuation and correlation phenomena in stable laser beams are being studied both theoretically and experimentally, using counting and analog techniques. Experiments have been completed to study the modification of these properties in scattering from solids and liquids, including scattering from the neighborhood of critical point fluctuations in CO<sub>2</sub>.

3. Square Ring Laser Configurations (Alley)

NASA, ARO ARPA

The square ring laser configuration is of interest for the study of instabilities and mode locking and mode cooperation phenomena, the propagation of light in moving media including

the measurement of the second-order Fresnel drag coefficient, and the factors limiting the ultimate sensitivity of such a configuration for the sending of small rotation rates. Ring lasers of five and twenty meter perimeters have been studied and the extension to forty meters is in progress. A method of controlling the sense of unidirectional spectrum using a magnetic field has been discovered.

4. Pulse Techniques

(Alley)

NASA, ARO, ARPA

Experimental measurements using a shielded and compensated solenoid are being made on the various relaxation processes, including wall relaxation and the "light shift" in rubidium vapor. The technique involves pulse techniques of the "spin echo" type. The use of a semi-conductor laser for optical pumping of alkali vapors is being explored.

The propagation of very short pulses of light in matter and the accompanying precursor waves has been examined theoretically and a search for a suitable medium to display the effect experimentally is in progress. To this end a sub-nanosecond optical pulse generator using mode locking techniques is being constructed.

5. Stimulated Raman Scattering

(Alley)

NASA, ARO, ARPA

The experimental verification of the predicted threshold for stimulated Raman scattering in nitrogen is under continuing examination. Modifications in our ruby laser to produce greater radiance using a master oscillator, power amplifier configuration are in progress. The phenomenon of self-focusing is being examined as a means of observing the effect.

6. Laser Ranging Applications

(Alley)

NASA, ARO, ARPA

Laser ranging applications include the experimental study of backscattering from the upper atmosphere (60 to 150 km), presumably from micro-meteorites, using the University of Maryland 20 inch telescope and a 10 joule,  $10^{-8}$  second Q-switched ruby laser. The principle investigator role has been undertaken in



in the design of an optical radar experiment to study the earth-moon system by ranging to optical retro-reflectors soft landed on the moon. In collaboration with scientists at the University of California at Los Angeles, University of Colorado, Wesleyan University, Princeton University and at the Goddard Space Flight Center, the technique is being developed as an Apollo Lunar surface experiment to increase knowledge in geophysics, selenophysics, celestial mechanics, relativity, and cosmology.

7. Long-Life He-Ne Gas Lasers  
ONR, ARPA

(Hochuli)

In 1964 we proposed to develop ultrastable Helium-Neon gas lasers. Relative frequency stabilities of the order of 1 part in  $10^{11}$  can be expected. This figure assumes that we are justified to extrapolate thermal expansion curves of some of the most suited materials such as Corning ULE or Owens Cervit.

These ideas became only practical if He-Ne gas discharge tubes with long life could be developed.

Our cold cathode research has produced three suitable cathode materials, namely Al, Be and Zr. The relevant properties of type 2024 Al cathodes have been published, the ones of Be and Zr will follow as soon as enough data is available. He-Ne discharges using properly dimensional cold cathodes can live in excess of 35,000 hours and Zr cold cathodes may turn out to be a cheaper substitute for Be.

B. SYNTHESIS AND STRUCTURE OF MATERIALS

1. Diffusion through Polymer Films  
NASA

(Smith)

A three-year project to evaluate diffusion data for polymeric systems has been completed and a final report written. A reactor has been designed and is being constructed to study the photochemical formation of very thin polymeric films. This work is part of the Ph.D. research of V. Coonahan.

2. Conformations and Relative Stabilities of  
Unsaturated Hydrocarbons  
NSF, ARPA

(Staley)

The major research activity of this group is concerned with two closely related parallel studies; a theoretical study involving the calculation of the conformations and relative stabilities of unsaturated hydrocarbons using the classical mechanical approach of enthalpies and free energies of isomerization of substituted cycloalkenes. The purpose of these studies is to define more precisely the relative contributions of the intramolecular forces which determine conformations and energies of isomerization.

In a project somewhat related to the above (which involves carbon-ionic intermediates) we have conducted an extensive study of the structure and alkylation reactions of cyclic pentadienyl anions. This study has produced the first definite correlation of reactivity and charge distribution in highly reactive ions, as well as interesting data concerning ion pairing effects.

A number of other diverse projects are underway or have recently been completed. Deuterium exchange and alkylation experiments with highly unsaturated bicyclic hydrocarbons have given evidence for a "bicyclohomoaromatic" intermediate; this species is the first example of a new type of aromatic system. In another study, the mechanism of the thermal reorganization of bicyclo [6.1.0] nona-2,4,6-trienes to *cis*-8,0-dihydroindenes has been elucidated. This interesting reaction apparently proceeds by a pathway which is, in part, formally "symmetry forbidden." Other related reactions are currently under investigation.

3. Fragmentation Processes by Electron Impact  
NSF, ARPA

(Staley)

We have recently become interested in fragmentation processes which are undergone by organic ions formed by electron impact in a mass spectrometer. One study has delineated some of the structural factors which are important in the fragmentation of hydrocarbons. A recent study of 1,3-propanediols has shown that the restriction of rotational degrees of freedom (as determined by conformation analysis using nuclear magnetic resonance and infrared spectroscopy) can have a significant effect in certain mass spectrometric fragmentation reactions.

Other projects include a study of the E reaction, in which a quantitative value for the preference of *trans* over *cis* elimination (ca. 6.6 kcal/mole) has been obtained for the first time, and a study of the steric and electronic factors involved in anionic cyclopropyl cleavage reactions.

4. Dynamic Structures of Solids

(Miller)

Petroleum Research Fund and ARPA

Nuclear Magnetic Resonance. Broadline nuclear magnetic resonance (NMR) is being used to study the dynamic structure of solids. The shape of the NMR signal of a solid is particularly sensitive to motions occurring at a rate of the order of  $10^5$ - $10^6$  sec<sup>-1</sup>, and thus broadline NMR is very useful for studying the onset of reorientation of molecules or complex ions in solids as well as for studying diffusion in solids. Emphasis is being given in this work to the study of the correlation of molecular reorientation in solids. It has already been shown that general reorientation about the center of mass is a cooperative phenomenon in RbPF<sub>6</sub> (PF<sub>6</sub> ion reorientation) and in crystalline CF<sub>4</sub>.

A versatile broadline NMR spectrometer has been constructed and is in operation. Molecular crystals in various stages of study currently include SiF<sub>4</sub>, PF<sub>5</sub>, cyclopropane, and spiropentane.

A special 4.2°-300°K NMR cryostat was designed to extend the temperature range over which molecular crystals may be studied, and should be operating early in 1969.

5. Bonding and Structure of Elements of Groups IV and V

(Bellama)

NSF, ARPA

The participation of the d orbitals in bonding of the Group IV and Group V elements is being investigated. Although the physical, structural, and chemical properties of e.g., monohalo derivatives of silicon, germanium, and tin compounds are in many respects very similar to those of their carbon analogues, the various properties often differ greatly from their carbon analogues and among themselves. Investigations to date suggest that (p+d) $\pi$  bonding is one of the most significant causes of the differences in the properties of the compounds studied.

The presence of similar backbonding in compounds of other Group IV and Group V elements is disputed. The present study should help to resolve backbonding properties of these elements.

Several isomeric series of compounds are currently being synthesized and examined by means of nuclear magnetic resonance, dipole moment and infrared vibrational studies. Evidence obtained is consistent with the postulated occurrence of (p+d) $\pi$  bonding from certain substituents to a silicon or germanium atom located in the alpha position. In addition, across-space interaction to silicon atom in the beta position or beyond is also indicated.

6. Synthesis, Structure and Degradation of Polymers

(Bailey)

ARMY, GOODYEAR, NASA, NIH, NSF

The research program can be divided into several areas:

1. The Synthesis of New Polymeric Materials
2. The Mechanism of the Thermal Degradation of Polymeric Materials
3. The Correlation of Chemical Structure with Physical Properties of Polymers

In the first area, the Diels-Adler reaction has been used to synthesize a series of ladder, or double-chained, polymers with unusual chemical and thermal stability. One objective is the synthesis of polynuclear aromatic ladder polymers that will be similar to graphite in thermal stability and electrical properties. Similarly, condensation reactions have been used to prepare spiro polymers with high thermal and chemical stability. Finally, the synthesis of a variety of new monomers has allowed us to prepare a series of new linear polyamines, polysulfides, and polydienes.

Although there is a great deal of knowledge available on the temperature at which polymers decompose thermally, very little information was available on the actual chemical reactions involved in such a breakdown process. We have been able to identify the actual chemical reactions in the thermal decomposition of a variety of polymers including polyethylene, polypropylene, polyisobutylene, polyacrylonitrile, and polystyrene. This has led us to identify the weak spots in a number of these polymers. It is hoped that such a study will lead to the design of much more thermally stable materials.

Finally, the synthesis of new monomers and polymers has allowed us to prepare a number of interesting materials. For example, the synthesis of amine-terminated polymers has allowed the convenient synthesis of polyurethanes and epoxies that have interesting structures. Finally, the synthesis of monomers such as glycidyl azide has allowed us to produce new polypeptides of unusually high molecular weight. The synthesis of new polymers with unusual structures has contributed greatly in understanding of the relationship of chemical structure and properties of the polymers.

7. Radiation Studies  
AEC

(Silverman)

Radiation induced luminescence. We have almost completed the measurements of the intrinsic efficiencies of  $\text{ZnS:Cu}$ ,  $\text{YVO}_4\text{:Eu}$ ,

and uranium borosilicate glasses for the conversion of 100, 200, and 350 keV electrons to light. Also, the absorption and scattering and absorption coefficients have been determined from reflectance measurements.

Graft polymerization by Gammas. We are continuing to measure the kinetics of grafting of styrene to long-chain alkanes.

Pulse radiolysis. We are measuring the mechanism of diene formation using single crystals of normal alkanes. The crystals have been obtained from NBS.

Dr. M. J. Kniedler has completed his dissertation on the calculation of dose-depth curves produced by electrons absorbed in multilayer targets.

8. Structure and Properties of Phosphorous Coordination Compounds (Grim)

AFOSR, NSF

The objective of this research project is to study the preparation, properties, and structural and bonding aspects of phosphorus coordination compounds by physical measurements such as X-ray diffraction, proton and phosphorus nuclear magnetic resonance, infrared spectroscopy, etc. Spectroscopic data has been correlated with various parameters such as bond strengths and molecular geometry.

9. Chemical Crystallography (Stewart)  
ARMY (Walter Reed), ARPA

This research effort can be described in three sections: First is the establishment of a system of crystallographic computer programs, called XOray-67, to automate the processing of crystal diffraction data. These include preparation of input data for diffractometers, processing the raw diffractometer data, processing photographic data, structure factors, least squares, Fourier transforms and many others. This system is maintained and enlarged regularly and has been partly programmed for the "new generation" of computers. It includes detailed write-ups and is now in use on UNIVAC, IBM and CDC computers throughout the world. Second is the determination of the detailed structure of a miscellany of selected compounds utilizing X-ray-67. This work has been carried out in collaboration with others in this department and elsewhere...One compound with Prof. Grim, one with Professor Reeve, one with P. K. Iber at Walter Reed, and one with C. Dickinson at N.O.L. Currently under support of the Bio-chemistry Division of the Walter Reed Army Medical Center we have installed an automated diffractometer. This is being used to solve structures of anti-malarials in order to relate physical structure to biological activity. Third is the overall aim to establish programs to solve

structures of fragments of, or compounds of, biological activity. We hope thereby to be able to aid biochemists with improvement in activity or decrease in toxicity of drugs. The overall goal is to relate structure to function through a detailed knowledge of the structure of the solid crystalline material. Connected with this effort is the problem of the collection of data and its processing which we now have automated. X-ray-67 is a useful tool in the processing, but a very great effort will be necessary to make routine the process of the structure analysis of solid compounds of biological activity.

### C. HIGH PRESSURE STUDIES AND EFFECTS

1. Galvanomagnetic Studies on Semi-Metals and Semi-Conductors at High Pressure (Spain)  
AEC, ARPA

Galvanomagnetic effects in graphite and lead telluride are currently being measured at ambient pressure. Apparatus to extend the measurements to hydrostatic pressures of 10 k.b. is nearly complete. Effects to be measured include the Hall Effect, magnetoresistance and oscillatory effects at low temperature. Thermomagnetic effects will be studied at ambient pressure.

The velocity of ultrasonic waves in graphite is being measured at hydrostatic pressures up to 10 k.b. (A joint study with Dr. L. Skolnick)

2. Vibrational Spectra of High Pressure Solids (Lippincott)  
ARMY (Durham), ARPA

Progress is represented both by completion of several initial projects and simultaneous expansion into other fields of interest. Two of the investigations have been completed successfully with the awards of Ph.D. degrees. The first of these concerns vibrational spectra of high pressure solids. Using high pressure techniques, crystal structures of solid modifications of ambient liquids have been determined, and a vibrational assignment of the simple coordination compound  $\text{BF}_3\text{-NH}_3$  has been made. Through this work, the usefulness of diamond cell instrumentation coupled with laser Raman and infrared spectroscopic techniques has been demonstrated.

The second study involved laser excited Raman spectroscopy of solids including studies on oriented single crystals, and on

high temperature and high pressure phase transitions. Both He-Ne and argon ion lasers were used to perform a variety of Raman experiments with these solids. An assembly was constructed to permit recording Raman spectra of materials at elevated temperatures on the Cary 81 monochromator. The red to yellow phase transition occurring in  $\text{HgI}_2$  at  $126^\circ\text{C}$  and 1 atmosphere was studied with this device. Raman spectra obtained at high pressure were similar to those obtained at elevated temperatures. This observation verified the similarity of high temperature and of high pressure, yellow  $\text{HgI}_2$ . These results in conjunction with other high pressure data have resulted in a new interpretation of the Raman active modes of vibration for the two solids of  $\text{HgI}_2$ .

Laser-excited Raman spectra have been obtained of various solid materials while subjected to very high pressure. Opposed diamond anvil pressure cells and commercial Raman spectrometers have been used for these experiments. Such Raman data provide a very sensitive probe for determining the effects of high pressures on the structure of molecules and on chemical bonds. The new techniques complement previously developed methods for obtaining visible and infrared spectral data, X-ray diffraction data, and optical microscopic data on pressurized samples.

3. Pressure Studies of the de Haas-van Alphen Effect (Anderson)  
ARPA

Studies of the changes in Fermi surfaces with pressures have been made in lead and graphite at pressures up to 4 kilobars. Similar studies in indium are presently being carried out. Studies of the changes with pressure in the Fermi surface of graphite have been completed and the work has been written up. In lead, indium and aluminum additional pressure studies have been made which are being used to test model potential calculations. These three supposedly quite similar metals exhibit quite different pressure effects which, however, seem to be describable in terms of the present pseudo-potential calculation. Pressure measurements in thallium are being started.

D. STUDIES OF SUPERCONDUCTING MATERIALS

1. Phase Transitions between Normal and Superconducting States (Glover)  
DOD

Experimental studies are being made of the phase transition

between the normal and superconducting states of a metal. An intrinsic temperature width of the transition as well as a systematic lowering of the transition temperature with decreasing sample thickness has been found. Effects of a magnetic field and of paramagnetic impurities are being studied. In another project shifts in the superconducting transition temperature and normal-state conductivity produced by electrostatic charging of thin metal films are being investigated. Results can be qualitatively understood on a density of states picture. Transition temperature shifts are found to depend linearly on the surface charge density. The results of the direct charging measurements make possible determinations of the surface charge density associated with the interface between an insulator and a metal. The technique is being used to study the formation of oxide layers on metals.

Work is also being done on the penetration of magnetic flux through superconducting films. Investigations of a superconducting phase of beryllium are being carried out.

2. Microwave Surface Impedance of Superconductors

(Koch)

DOD

Microwave Surface Impedance of Superconductors in a Weak Magnetic Field: At finite temperature excited quasi-particle states in superconductors form magnetic field induced surface states that are in many respects similar to those observed in the normal state. The microwave absorption spectrum for superconducting Sn, In and Pb show distinct peaks at a value of field where the energy of the bound state equals the microwave photon energy. The peak results from resonant transitions between the field induced surface state and states at the bottom of the gap of the B.C.S. spectrum. We have been concerned with studying the microwave absorption spectrum in crystals of Sn, In and Pb, with a view toward learning more about the surface states in the superconductors. A study of the absorption peaks should yield detailed information on such parameters of the penetration depth  $\lambda$ , velocities of normal electrons and lifetimes of the quasi-particle states.

3. Electromagnetic Properties of Superconductors

(Leibowitz)

ARPA

Type II Effects in Elemental Superconductors. An experimental investigation of type II superconductors is being actively continued. During the period of this report a study of the isolated



vortex state in superconducting vanadium has been completed, and the results reported. It was found possible in the aforementioned work to study the properties of individual vortices, which populate type II superconductors at fields lying between  $H_{C1}$  and  $H_{C2}$ , by studying the absorption of compressional ultrasonic waves in pure vanadium as a function of magnetic field and temperature. From simultaneous measurements of the ultrasonic attenuation and magnetization the scattering width of the vortex for quasiparticles was found to be  $(2.4 \pm 0.4) \times 10^{-6}$  cm for temperatures near  $T_C$ . A recent calculation is in excellent agreement; the scattering length is determined to be  $2.1 \times 10^{-6}$  cm. It is planned to continue this work in high purity niobium. Further, we plan to investigate the electromagnetic interaction of ultrasonic shear waves with excited electrons near the so-called upper critical field,  $H_{C2}$ , in niobium satisfying the condition  $\ell \gg \lambda$ ; here  $\ell$  is the electron mean free path and  $\lambda$  the ultrasonic wavelength.

**Electromagnetic Properties of Superconductors.** We have completed a series of experiments designed to characterize a new absorption phenomenon which we have observed near  $T_C$ , the superconducting critical temperature in high purity indium. A phenomenological model has been devised. According to the model and the experimental evidence in indium, the absorption anomaly reflects the relaxation of the order parameter in the superconductor; the experiment affords an excellent method for studying the Ginzburg-Landau order parameter and its temperature dependence near  $T_C$ . It has been determined that this relaxation time  $\tau \sim 10^{-9}$  sec within about 2 millidegrees of  $T_C$  in indium, and is consistent with a temperature dependence of the form  $1/T - T_C$  near  $T_C$ . The experiments will continue in indium, tin, and other type I superconductors.

**Hypersonic Measurements on Elemental Metals.** The first data exploring the electromagnetic interaction region at  $10^9$  sec $^{-1}$  have been obtained. The initial observations were made in high-purity, oriented tin specimens having thickness  $\sim 10^{-4}$  mm. It is hoped that the experiments will comment on the predictions of Cullen and Ferrell related to the temperature dependence of the absorption of transverse phonons near  $T_C$ , and show explicitly the frequency dependence of the response function describing the electrodynamic properties of a superconductor.

**Strong-Coupling Effects on the Lattice-Wave Absorption near the Superconducting Transition.** In this program, the purposes of which were outlined in the last report period, we have finally succeeded in obtaining experimental information in the temperature range for which ultrasonic absorption anomalies in the so-called strong-coupling superconductors have been reported. The present data extends the frequency range by approximately a factor of 10 over previous work

reported in the literature; it is hoped that the correspondingly increased range of  $ql$  thereby made available will shed light on the reported anomalies, here  $q$  and  $l$  are the phonon propagation vector and electron mean free path, respectively.

4. Thermal Conductivity of Superconductors  
ARPA

(Bhag<sup>2</sup>\*)

The thermal conductivity of strong coupling superconductors (e.g. Hg) has been investigated in the temperature range 1.15°K to 4.5°K. Anisotropy in conductivity has been discovered. The results have been explained in terms of low lying peaks in the phonon spectrum.

E. MECHANICAL PROPERTIES OF METALS AND ALLOYS

1. Models of Alloys  
NSF and ARPA

(Bolsaitis)

The study of various interionic potentials and their relationship to measured elastic constants, their pressure derivatives, lattice parameters and cohesive energies for the noble metals and their alloys is nearing its completion. It has been found that no physically reasonable exchange potential can give a complete and self consistent description of the elastic properties of the noble metals without the inclusion of some contribution from the Fermi energy to the shear model and their pressure derivatives. This confirms the results of other experiments which indicate that the Fermi surface of all three noble metals may be touching the Brillouin zone boundary.

An analysis of the net pairwise potentials on the basis of the electron cell model of alloys indicates that in order to obtain minimization effects of the energy of mixing with respect to volume of mixing, static displacements and short range order, a short range attractive force, e.g. Van der Waals, is necessary in addition to the repulsive interionic exchange interaction.

The results of this study have been applied to the calculation of energies of formation of noble metal alloys, vacancies and order-disorder transformations. Two papers related to this work have been presented and a more comprehensive one will be forthcoming in the near future.

The continuation of this study will deal with further details of the contributions of the Fermi energy and hybridization of electron orbitals to the elastic properties of metals since these contributions are important for the extension of the electron cell model to metals and alloys of higher valency.

2. Short Range Ordering

(Asimow)

ARPA, AEC

The kinetics of short range ordering in Ag-Au alloys are being studied by resistivity methods. Small diameter alloy wires are quenched from various temperatures and then the annealing kinetics are studied as a function of annealing temperature. The activation energy for vacancy motion and formation as a function of alloy content is being determined as is the activation energy for the ordering process. A computer model of the ordering process is being developed for comparison with experimental results.

3. Solid Solution Hardening

(Asimow)

AEC, ARPA

Experimental and theoretical work on the mechanisms by which the critical resolved shear stress (CRSS) is increased in fcc solid solution alloys are being undertaken. The effect of short range ordering on the Ag-Au system has been experimentally investigated by testing annealed single crystals, then quenching them and retesting. Preparations are underway for an experimental determination of the CRSS as a function of temperature down to 4.2°K. A theoretical investigation of the size and modulus defect interaction with a dislocation has been completed and a theoretical study of the temperature dependence of the CRSS along somewhat different lines than the usual theories is underway. The theoretical analysis to date shows excellent agreement with the CRSS data available for alloy single crystals extrapolated to 0°K. Additional work involving the change in resistivity with deformation of gold-silver alloys and a study using etch pit techniques of dislocation density changes when alloying is underway.

4. Deformation of Materials  
ARPA

(Armstrong)

The influence of dislocations, subgrain boundaries and grain boundaries on the hardness of metals is being investigated. The limiting strength which can be achieved by polycrystal grain size refinement is being investigated experimentally and theoretically. A study is being undertaken to determine the properties of dislocation pile-ups in a stress-gradient such as occurs in simple bending or bending fatigue. Various constitutive relations for crystal plasticity which derive from dislocation theory are being studied in respect to developing a general theory for the transition from ductile to brittle behavior exhibited by polycrystalline body-centered cubic and hexagonal close-packed metals.

X-ray diffraction contrast microscopy - A dynamical theory approach to the Berg-Barrett X-ray technique is being developed with Prof. B. Roessler of Brown University. The Berg-Barrett X-ray technique is being applied to zinc crystals subjected to chemical and thermal heat treatments in collaboration with Prof. J. M. Schultz of the University of Delaware.

5. Electron Cell Model of Alloys  
ARPA, OSW

(Skolnick)

A simple method for calculating vacancy formation energies in metals and alloys based on the Electron Cell Model has been developed. This model differs from that considered by Cheng, Wynblatt and Dorn in that the effect of alloy concentration per se, rather than ordering effects, is the principal factor considered in the determination of the vacancy energy. The formation energies of vacancies and divacancies in pure noble metals and of vacancies in the alkali metals agree reasonably well with experimental results and other more complex calculations. In addition, divacancy energies in the alkali metals have been calculated. The results for vacancy energies in alloys show that the energy of their formations is dependent on the specific alloy system, and may be either larger or smaller than the formation energy in the pure metal components. This is in contrast to results obtained by Ramaswami and Tariyal based on another model.

6. Stress Corrosion Studies  
ARPA, OSW

(Skolnick)

Studies of the relative effects of preferred orientation and grain morphology on the directional susceptibility to stress corrosion cracking of a 7075-T651 aluminum alloy plate have been conducted. Preferred orientation was found to be of secondary importance when compared to the effect of grain morphology. A high degree of preferred orientation, rather than any specific slip plane orientations, was found to increase the susceptibility of specimens with the same grain morphology. The primary role of grain morphology was found to be in controlling crack propagation. Observations of cracking in as short a time as 30 seconds at grain boundaries normal to the applied stress on the surface of longitudinally stressed specimens showed conclusively that it is the slow rate of propagation along boundaries parallel to the applied stress, and the fact that the intergranular crack must propagate primarily in this direction, that accounts for the low susceptibility of longitudinally stressed specimens. Pitting corrosion was found to occur to a much greater extent on unstressed than on stressed (undergoing stress corrosion cracking) specimens. This phenomenon is explained by what is termed an "internal cathodic protection mechanism."

7. Fundamentals of Anodic Processes  
OSW, ARPA

(Skolnick)

The combined use of ultrahigh vacuum, ellipsometry, and a gas plasma electrolyte provides a direct means to examine the growth mechanism of thin oxide films. From the preliminary results that are presented here, it appears that the VEP technique can be used to provide further information on the initial stages of oxidation, the effect of impurities on film growth kinetics, and the structure of passive oxide films.

In addition the possibility exists that coatings can be formed that possess properties that differ from materials produced by more conventional techniques.

8. Irradiation Strengthening of b.c.c. Metals and Solid Solutions  
AEC and ARPA

(Arsenault)

There have been numerous investigations of the rate-controlling mechanism for deformation in neutron-irradiated face-centered

cubic metals, but there have been only a few preliminary experiments employing body-centered cubic metals. These experiments indicate that the neutron damage does not appear to change the rate-controlling mechanism of slip in b.c.c. metals. The reason for the absence of a change is due to the intrinsic rate-controlling mechanism of slip in b.c.c. metals and the particular experimental conditions employed.

These reasons are examined in detail and the probable experimental condition necessary for the observation of a detectable change in the rate-controlling mechanism is explored.

#### F. OPTICAL AND SPECTROSCOPIC PROPERTIES OF METALS

##### 1. Laser Raman Spectra of Piezoelectric Crystals (Khanna) ARPA

Much of the effort has gone into the study of the Raman spectra of some piezoelectric (non centro symmetric) single crystals employing laser excitation. One expects to find in the spectra of such crystals some additional information on the longitudinal phonons. In particular, the Raman spectra of one crystalline modification of glycine (r-glycine) were investigated in detail. Some of the observed phonons do split into transverse and longitudinal phonons as found in the present studies. Some of the early measurements have given an apparently erroneous assignment to these observed phonons. Cesium nitrate is another non centro symmetric crystal investigated in detail (in collaboration with Dr. Alvin J. Melveger). The detailed analysis of the spectra of  $C_6H_5NO_2$  has enabled us to establish more or less with certainty the space group symmetry of this crystal. All the observed phonons have been assigned; no anisotropy in the spectra of these crystals has, however, been found.

##### 2. Vibrational Spectra of Solids (Lippincott) PHT, PHR and ARPA

Single crystals of a series of double metal sulphates have been grown in the laboratory using a simple evaporation technique. These are being studied by Raman and by low temperature infrared techniques. The results are being analyzed and will be published in the near future.

Studies are in progress using polarized infrared and Raman spectra of accurately oriented single crystals of molecular solids. Intermolecular potential functions will be determined from studies of lattice vibrations, and correlations of these potential functions with macroscopic properties of the crystals will be sought. Also, separation of the static and dynamic contributions to the intermolecular potential function are being derived.

Laser excited Raman spectra of  $\text{Co}(\text{CO})_3\text{NO}$  have been obtained and interpreted with a reassignment of fundamentals. Symmetry force constants have been calculated from reported vapor phase frequencies.

Our research project on laser induced Raman spectra of some tungstates and molybdates has been completed. Raman spectra of single crystals of  $\text{CaWO}_4$ ,  $\text{CaMoO}_4$ ,  $\text{PbWO}_4$ , and  $\text{PbMoO}_4$  have been obtained using a He-Ne and an Argon ion laser for excitation. Polarization data have enabled us to assign unambiguously the observed fundamentals as the Raman active species of the point group  $C_{4h}$  to which these crystals belong. Comparison of spectra of these crystals in the low frequency region has also enabled us to make an approximate classification of the bands as rotational or translational lattice vibrations.

### 3. Spectral Studies of Absorbed Species

(Lippincott)

ARPA, NATO

Samples absorbed in experimental glass matrices have been investigated using the Cary 81 spectrophotometer. Attempts are underway to obtain Raman spectra of a monolayer of  $\text{CCl}_4$  in such a matrix. This project is still in a very early stage and a more extensive investigation is planned. Spectra of various other samples have been obtained in isolated experiments but these are not part of any detailed or complete study. A new spectrometer is presently being constructed to facilitate work on single crystal samples.

### 4. Optical Properties of Gold and Other Metals

(Beaglehole)

ARPA

Studies of the optical properties of metals and insulators have continued during 1968. (1) Careful measurements of the reflectivity of gold in the region 1.5 to 6 eV, and of the changes in this reflectivity when small amounts of iron and silver are alloyed have been made. These measurements have allowed us to evaluate the

the changes in energy and lifetime of the electrons in gold induced by the impurities. (2) We have studied the reflecting properties of a metal grating, elucidating especially the occurrence of the so-called "Wood's Anomalies", which arise from waves of electron charge propagating on the metal surface. The setting up of experiments on (3) the Piezo-reflectance of metal single crystals, (4) magneto-optic effects in simple metals, and (5) excitons (5) excitons in solid xenon, has continued.

5. Optical Properties of Alkali Metals (Bardasis)  
ARPA, AFOSR

Work is currently being done with Mr. Aram Karakashian on the optical properties of the alkali metals. Progress shows the important effects of phonon assisted transitions in correctly determining the experimentally obtained absorption in the optical photon range. The field theoretic calculation also includes the self energy effects due to electron-electron interactions. We hope to complete this work by the end of the 1968-69 academic year.

G. MAGNETIC AND ELECTROMAGNETIC PROPERTIES OF MATERIALS

1. Electronic Structure of Small Molecules (Ginter)  
ARPA

This project is one of continuing research effort on the electronic structure of small molecules of theoretical and astrophysical interest. In particular, several studies on the Rydberg states of  $H_2$  and  $He_2$  were completed and additional progress has been made on the Rydberg "f complexes" of NO and the  $npII_u$  series in  $D_2$ . Experimental studies (primarily more development) on several small free radicals have been initiated).

2. Effect of Electron Interactions on X-ray Emission Spectra of Metals (Glick)  
ARPA, AFOSR

This research was conducted while on sabbatical leave at the University of Paris at Orsay, France and in the Theoretical Physics Division of the Center for Nuclear Studies at Saclay, France. It concerns studies of electron interaction effects on



the soft X-ray emission spectrum of metals. In particular, renormalized forms of the theory are being studied in an attempt to understand whether certain divergencies appearing in the theory are related to observed structure in the spectra, and whether these effects can explain the differences between K and L shell spectra near the high energy edge.

### 3. Domain-Wall Mobility ARPA

(Myers)

We have studied the motion of a  $180^\circ$  domain-wall in pure yttrium iron garnet as well as in ferrite system, using the Winter-Janak's domain-wall excitation spectrum. In particular, the domain-wall mobility as a function of temperature has been thoroughly studied. We examined various possible relaxation processes and showed that the two-body part of the depolarization energy due to the surface roughness of the sample where the domain-wall plane crosses the sample surface is the main source of resistance to domain-wall motion in pure yttrium iron garnet. The four-body interaction intrinsic process contributes very little even at higher temperatures (about 10% of the two-body interaction at  $300^\circ\text{K}$ , much less at lower temperatures). For a checker-board like surface corresponding to grit diameter  $R \approx 0.25\mu - 0.30\mu$  ( $\mu = 10^{-4}\text{cm}$ ), it is found that the wall mobilities are 720, 740, 1200 and 5000 cm/sec-oe at 4.2, 77, 195 and  $300^\circ\text{K}$ , respectively. These numbers are in good agreement with the experimental data reported by Wanas, and Hagedorn and Gyorgy and we visualize domain-wall motion relaxation taking place in the following way: A domain-wall is set in motion when a small, uniform external field is applied along an easy axis. To first order, only the uniform translational domain-wall magnon mode is excited. This mode is immediately disturbed by the surface depolarization energy which is non-uniform and extends well into the matter, causing transition from the uniform translational domain-wall magnon mode to non-uniform modes and breaking up uniformity of the precessional motion of spins. As a result, precessional motion of spins become dephased and randomized and domain-wall motion is forced to slow down. The four-body interaction intrinsic processes also help randomizing these spins, but only in small measure.

Pseudo-dipolar fluctuation effects are insignificant in YIG but it is important in ferrites with an inverted spinal structure. Assuming (on basis of ferromagnetic resonance data) the fluctuation field is about  $10^5$  oe at  $0^\circ\text{K}$  and taking into account its possible temperature variation, we showed that this along with the surface roughness effects combine to yield the same order of wall mobilities as Dillon and Earl experimentally observed in manganese ferrite.

Finally, research is currently in progress about domain-wall mobility in silicon-doped yttrium iron garnet.

4. Superconducting Dielectric Constant (Bardasis)  
ARPA, AFOSR

The calculation of the absorptive part of the superconducting dielectric constant at low temperatures and frequencies begun last year has been completed and is currently being written up for publication.

5. Superfluid Liquid Helium (Bardasis)  
ARPA, AFOSR

Theoretical problems associated with the experiments on the superfluid aspects of liquid helium are being carried out. In particular, the role played by fluctuations in the superfluid density when the temperature is close to the transition temperature is being examined.

6. Critical Heat Flux and Second Sound in Liquid Helium II (Bhagat)  
ARPA

The critical heat flux in liquid helium II has been investigated at temperatures close to  $T_\lambda$ . The kinetics of the  $\lambda$ -transition in the presence of a heat current is now being investigated in greater detail.

Experiments are being initiated to study the velocity of second sound in liquid helium II at temperatures near 2.173°K. Phenomena concerned with the phase transition will be investigated.

7. Pressure Dependence of Elastic Constants (Bolsaitis)  
ARPA, NSF

The equipment for the measurement of the pressure dependence of elastic constants by the pulse superposition method has been assembled and is currently being tuned and adjusted.

Initial measurements will be made on gold-copper alloy single crystals of various compositions and degrees of order to determine the relationship of the interionic potentials in alloys to those in the pure metals.  $\text{Cu}_3\text{Au}$  alloys single crystals of varying degrees of order are currently being prepared for the aforementioned measurements.

8. Refractory Oxide Electrolytes  
ARPA, NSF

(Bolsaitis)

This project has the dual purpose of preparing and studying ceramic materials of high ionic conductivity and to use some of these for thermodynamic measurements in solid electrolyte emf cells.

Currently an ultra high temperature furnace is being assembled for the sintering of ceramic oxides and the measurement of their conductivity. A series of ternary refractory oxide mixtures, e.g.  $ZrO_2$  -  $HfO_2$  -  $CaO$ ,  $ZrO_2$  -  $Y_2O_3$  -  $BeO$  will be examined for size and valence effects on their vacancy concentration and ionic and electronic conductivities.

The first thermodynamic measurements are being made on a ternary Cu-Au-Ag alloys in an emf cell using  $ZrO_2$  -  $CaO$  as the electrolyte.

9. Microwave Surface Impedance  
ARPA, DOD

(Koch)

Electrons in metal crystals in the presence of a magnetic field are bound to the surface region in quantum mechanical states. These magnetic field induced surface states correspond to classical electron trajectories skipping along the metal surface by periodic specular reflection. Transitions between such states account for the curious impedance oscillations in fields between 0-100 Oe that have been observed. We study such low field oscillations in crystals of Sn, In, Al, Ga, as well as semi-metals Bi and Sb. The effect gives information on dynamical properties of electrons at a single point on the Fermi surface. Linewidths and lineshapes of the oscillation signals are a measure of the probability of specular reflection of an electron at the metal surface.

A second project concerns electrodynamics of metals at submillimeter wavelengths. The project centers on the development of a suitable infrared laser-source and techniques for measuring surface impedance at high frequencies. Specifically we plan to investigate the field induced surface states and cyclotron resonance in a regime of frequency and fields where interesting and new aspects will become apparent.

10. Helicon Waves in Metals  
ARPA, DOD

(Koch)

We have been concerned with a study of helicon waves in single crystals of In. For the [001] direction we have discovered a propagation window for helicons below the cyclotron damping edge. The existence of this region of undamped propagation at magnetic fields below the edge is a reflection of the peculiar variation of  $dA/dk_H$  with  $k_H$  for this particular direction in In. The effect measures  $dA/dk_H$  at particular points on the Fermi surface. When the magnetic field is tilted away from perpendicular to the surface helicon waves are attenuated by groups of electrons traveling along H with the phase velocity. This effect is being studied in In to obtain detailed information on Fermi surface geometry.

11. de Haas-van Alphen Effects  
ARPA

(Anderson)

A detailed study of the de Haas-van Alphen (dHvA) effect in indium is being carried out in order to understand the electronic structure of indium and to map out the Fermi surface. The field modulation technique is used with a 55 K Gauss superconducting magnet. The results are being compared with a parameterized pseudo-potential model which describes the Fermi surface of indium in terms of a few orthogonalized plane waves. It has been found that six orthogonalized plane waves describe the present indium Fermi surface data quite well. A preliminary report of this calculation is described in the technical report, The Parameterized Pseudopotential Model for the Fermi Surface of Indium. Accurate measurements of the high frequency dHvA oscillations have been made for crystals oriented along symmetry directions and these results have been published.

Small amounts of Bi and Tl (up to 2%) have been added to lead, and single crystals have been grown to study the effects of alloying on the dHvA periods and amplitudes. Using nuclear magnetic resonance techniques, we have been able to make accurate measurements of magnetic fields (0.01%) in situ. Therefore, we have been able to detect period changes in lead alloys with concentrations of only 0.1% bismuth. Preliminary results suggest that dHvA periods resulting from the third band electron surface decrease much more quickly than would be expected from the rigid band model.

A program has been started to study Fermi surfaces of transition metals. The initial problem has been one of sample preparation. From some very pure starting material furnished by Dr. Robert Meyerhoff of Union Carbide Corporation, Linde Division, small single crystals of niobium

have been grown which should prove suitable for detailed de Haas-van Alphen measurements. Some preliminary studies of magnetoresistance have been made in niobium and vanadium. Present plans are to study magnetoresistance and Hall effect in vanadium in some detail.

12. Model Potential Calculations of Fermi Surface (Anderson)  
ARPA

Model potential form factors based on simple model potentials are being calculated for several nearly free electron metals. The results are used in band calculations, for example in the study of the effects of pressure on the Fermi surfaces of lead and indium. In addition to the band calculations, lattice dispersion curves are being obtained from the model potential approach. Elastic constants and their pressure derivatives are being studied. More complete band calculations using the Koringa, Kohn, Rostaker Green's function technique are planned for indium and perhaps other metals. A non-local pseudopotential model has been developed for FCC metals. This model has been used to study the Fermi surface and its pressure dependence for lead and appears to be quite successful.

13. Ferromagnetic Metals (Anderson)  
AEC, ARPA

Ferromagnetic resonance studies have been made in iron single crystal whiskers at temperatures between 300°K and 4°K in order to understand the contributions to the resonance linewidths as a function of temperature. Some results have been published. Studies of anisotropy effects in single crystal nickel disks have been started. A program for studying the hexagonal ferromagnetic metals, cobalt and gadolinium, is underway. Samples are being prepared for ferromagnetic resonance studies. A preliminary attempt has been made to observe dHvA oscillations in cobalt and very weak signals appear to have been detected. Fermi surface results will be used to interpret the ferromagnetic resonance results.

14. Ferromagnetic Metals  
ARPA, AEC

(Bhagat)

The phenomenon of resonant microwave absorption in ferromagnetic materials has been studied in Nickel single crystals at 22kMc/s and 33kMc/s over the temperature range of 20°C to 380°C. It has been demonstrated that the intrinsic relaxation parameter in Nickel is independent of temperature between 20°C and 200°C. At higher temperature several new results have been obtained. Further work is being initiated in Nickel and Cobalt.

15. Magnetic Impurities and Size Effects in Metals  
ARPA

(Falk)

Dr. Fullenbaum has finished his thesis consisting of calculations of spin correlation functions in a system consisting of an isolated magnetic impurity in a metal. The computations were done assuming s-d interaction using various approximate models.

We have been examining in detail ramifications of a relativistic Fermi surface model consisting of necks, spin orbits, hole orbits, etc., as manifested in helicon propagation and Gantmakher-Kaner oscillations.

16. Thermal Conductivity of Bismuth  
ARPA

(Bhagat)

The region of intermediate fields (100-1000 Oe) was investigated in further detail and results were reported at the 7th Thermal Conductivity Conference.

17. Correlations in Narrow Energy Bands  
AFOSR

(Prange)

Correlations in narrow energy bands, transport properties of interacting electron-phonon systems, resonant screening in metals, and magnetic surface levels are being studied, taking into account the correlations of electrons and the classification of their effects. Much progress has been made in the case of electron-phonon systems where a complete classification of the low energy effects have been achieved. In the case of correlation in narrow energy bands, there remains a great deal of work to be done and the problem is far from understood. A study has also been made of sharp resonances in the neighborhood of impurity atoms.

SECTION III  
FACULTY PARTICIPATING IN MATERIALS RESEARCH

<u>Name</u>	<u>Title</u>	<u>Department</u>
C. O. Alley	Associate Professor	Physics
J.R. Anderson	Assistant Professor	Physics
*R.W. Armstrong	Professor	Mechanical Engineering
R.J. Arsenault	Associate Professor	Chemical Engineering
R.J. Asimow	Associate Professor	Mechanical Engineering
G. Atkinson	Professor	Chemistry
W.J. Bailey	Professor	Chemistry
A. Bardasis	Assistant Professor	Physics
D. Beaglehole	Assistant Professor	Physics
J.M. Bellama	Assistant Professor	Chemistry
*S.M. Bhagat	Associate Professor	Physics
P. Bolsaitis	Assistant Professor	Chemical Engineering
D.G. Currie	Assistant Professor	Physics
D.S. Falk	Associate Professor	Physics
M.L. Ginter	Assistant Professor	Institute for Molecular Physics
A. Glick	Assistant Professor	Physics
R.E. Glover	Professor	Physics
S.O. Grim	Professor	Chemistry
J. Huheey	Associate Professor	Chemistry
R.J. Khanna	Assistant Professor	Chemistry
J.F. Koch	Associate Professor	Physics
V. Korenman	Assistant Professor	Physics
J.R. Leibowitz	Assistant Professor	Physics
*E.R. Lippincott	Professor	Chemistry

<u>Name</u>	<u>Title</u>	<u>Department</u>
*G.R. Miller	Assistant Professor	Chemistry
R.D. Myers	Professor	Physics
S.K. Poultney	Assistant Professor	Physics
R.E. Prange	Associate Professor	Physics
J. Silverman	Professor	Chemical Engineering
L. Skolnick	Associate Professor	Chemical Engineering
T.G. Smith	Associate Professor	Chemical Engineering
*I.L. Spain	Assistant Professor	Institute for Molecular Physics
S.W. Staley	Assistant Professor	Chemistry
J.M. Stewart	Professor	Chemistry
O.B. Verbeke	Assistant Professor	Institute for Molecular Physics

\*CMR Advisory Committee



SECTION IV  
RESEARCH ASSOCIATES

<u>Name</u>	<u>Department</u>
J.R. Allkins	Chemistry
A.R. Bandy	Chemistry
N. Berk	Physics
C.W. Brown	Chemistry
G.C. Das	Chemical Engineering
H.D. Drew	Physics
H.C. Duecker	Chemistry
P.R. Giffiths	Chemistry
B.R. Guscott	Chemistry
J.C. Hamer	Chemistry
I.J. Hyams	Chemistry
R.J. Jablonski	Chemistry
D. Jones	Chemistry
N. Kawabata	Chemistry
S.Y. Lee	Chemistry
M.S. Malmberg	Chemistry
R.H. Mann	Chemistry
D. Naugle	Physics
J.R. Osmundson	Physics
H.R.H. Patil	Chemistry
A.C. Sinclair	Physics
S.K. Tandon	Chemistry
L.S. Whatley	Chemistry
W.B. Willott	Physics
N. Wood	Chemistry

## SECTION V

### GRADUATE STUDENTS PARTICIPATING IN MATERIALS RESEARCH PROGRAMS

F. Ahern	Physics
W. Aldrich	Mechanical Engineering
J. Alishouse	Physics
G. Arnstein	Mechanical Engineering
G. Ausman	Physics
L. Baccei	Chemistry
F. Ballas	Chemistry
H. Beale	Chemical Engineering
C. Beam	Chemistry
J. Benson	Chemistry
A. Bhatnagar	Physics
S. Bierer	Chemistry
I. Block	Chemical Engineering
R. Bose	Physics
D. Boyd	Chemical Engineering
D. Bricker	Physics
J. Brown	Chemistry
S. Bruno	Chemistry
J. Buchanan	Chemistry
E. Burke	Physics
D. Capozza	Chemistry
E. Cappuccilli	Chemistry
J. Carolan	Physics
G. Cessac	Chemistry
Y. Chan	Chemical Engineering
R. Chang	Physics
F. Cheng	Physics
R. Chiarodo	Chemical Engineering
E. Chicklis	Physics
E. Conrad	Chemical Engineering
V. Coonahan	Chemical Engineering
D. Copeland	Chemical Engineering
T. Copeland	Chemistry
E. Davidoff	Chemistry
R. Davis	Physics
J. Davison	Chemistry
R. Doezma	Physics
R. Doherty	Chemistry
A. Edwards	Chemical Engineering
R. Einhorn	Chemistry

H. Eisen	Chemical Engineering
J. Erdman	Chemistry
G. Eubanks	Chemical Engineering
J. Feinberg	Chemistry
R. Ference	Chemistry
J. Fisher	Chemical Engineering
J. Fogt	Chemistry
M. Fullenbaum	Physics
W. Gerson	Physics
J. Glanville	Chemistry
R. Gsell	Chemistry
S. Gupta	Chemical Engineering
I. Haddad	Chemistry
D. Harris	Chemical Engineering
D. Hassan	Chemical Engineering
A. Hart	Chemistry
J. Heinze	Chemistry
J. Hennessey	Chemistry
T. Henry	Chemistry
B. Hinrichs	Chemistry
K. Hsieh	Chemical Engineering
H. Huang	Physics
O. Hunderi	Physics
V. Iyer	Mechanical Engineering
J. Jensen	Physics
P. Jindal	Mechanical Engineering
M. Joseph	Physics
A. Karakashian	Physics
M. Kaufman	Chemistry
R. Kerter	Chemistry
H. King	Chemistry
M. Kniedler	Chemical Engineering
C. Kuo	Physics
S. Lane	Physics
K. Lasala	Physics
J. Lephardt	Chemistry
S. Macajani	Mechanical Engineering
T. Maccarone	Chemistry
J. Maldonado	Physics
R. Marr	Chemistry
P. McAllister	Chemistry
J. McClure	Physics
C. McCormick	Chemistry
P. McCormick	Physics
J. McGarritty	Chemical Engineering

A. Melveger	Chemistry
P. Miller	Chemistry
P. Miller	Chemistry
R. Molenda	Chemistry
D. Morris	Chemistry
D. Nagel	Chemical Engineering
T. E. Nee	Physics
T. W. Nee	Physics
P. Nicholas	Chemistry
L. Norman	Chemical Engineering
R. Obremski	Chemistry
J. Osmundson	Physics
E. Page	Physics
J. Penar	Physics
W. Phillips	Mechanical Engineering
H. Plastas	Chemistry
R. Pohle	Physics
C. Poranski	Chemistry
R. Predmore	Chemical Engineering
A. Raghuram	Mechanical Engineering
D. Reichard	Chemistry
A. Rheingold	Chemistry
B. Riddhagani	Mechanical Engineering
J. Ritter	Chemistry
E. Robinson	Chemistry
J. Rocchio	Chemistry
M. Rothstein	Physics
P.K. Samal	Mechanical Engineering
P. Scharnhorst	Physics
R. Sebastian	Physics
M. Senyek	Chemistry
A. Serlemitsos	Physics
P. Sezeapanik	Physics
R. Sibbald	Physics
E. Silverberg	Physics
R.M. Singer	Chemistry
G. Singh	Physics
S. Singhal	Physics
G. Slawecki	Chemical Engineering
R. Smith	Physics
B. Statz	Chemistry
U. Strom	Physics
J. Svitak	Mechanical Engineering
H. Tamburin	Chemistry
D. Thomas	Chemistry
R. Thomas	Chemical Engineering

J. Trondsen	Chemical Engineering
W. Tseng	Physics
G. Ugiansky	Chemical Engineering
L. Ulmer	Chemistry
C. Vest	Chemical Engineering
S. Wandiga	Chemistry
P. Wang	Chemistry
G. Warner	Chemistry
P. Watts	Chemistry
C. Weiffenbach	Chemistry
K. Weiner	Chemistry
D. Wheatland	Chemistry
R.S. Williams	Physics
B. Winer	Physics
F. Wiseman	Chemistry
H. Yakowitz	Chemical Engineering
A. Yankowsky	Chemistry
T. Yolken	Chemical Engineering
J. Zeger	Chemistry

## SECTION VI

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